FACULTY OF ENGINEERING AND ARCHITECTURE

DEPARTMENT OF MATERIALS, TEXTILES AND CHEMICAL ENGINEERING

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KINETICS OF THE REDUCTIVE AMINOLYSIS OF GLUCOSE WITH DIMETHYLAMINE BELOW 400 K

RENEWABLE RESOURCES AS A MEANS TO INHERENT SAFETY

Cellulose pulp as a renewable resource for the production of aminoalcohols (N,N-dimethylaminoethanol, DMAE) and diamines (N,N,N',N'-tetramethylethylenediamine, TMEDA). These chemicals are currently made from ethylene oxide and dichloroethane.

Specific research goal: Development of a **competitive** , **greener** and **inherently safe** production process for **DMAE** and **TMEDA** by means of an **experimental** and **kinetic modeling** investigation of the **reductive aminolysis** of glucose, as a model component, with DMA as aminating agent

EXPERIMENTAL INVESTIGATION

fed-batch reactor

W_{cat}	2.9 – 7.4	g_{cat}
T	383 – 398	K
P	6.0 – 7.5	MPa
$n_{glucose}^0$	0.2 – 0.4	mol
$n_{H2}/n_{glucose}^0$	4.7 – 9.6	mol mol^{-1}
$n_{DMA}/n_{glucose}^0$	11.9 – 23.6	mol mol^{-1}
$F_{glucose}$	5 - 30	10^{-5} mol s^{-1}
Glucose concentration	500	$g_{glucose}$ l_{H2O}^{-1}

narrow range of operating conditions possible, given the **complex chemistry**, resulting in an **unstrained dataset** of 7 experiments and 36 data points

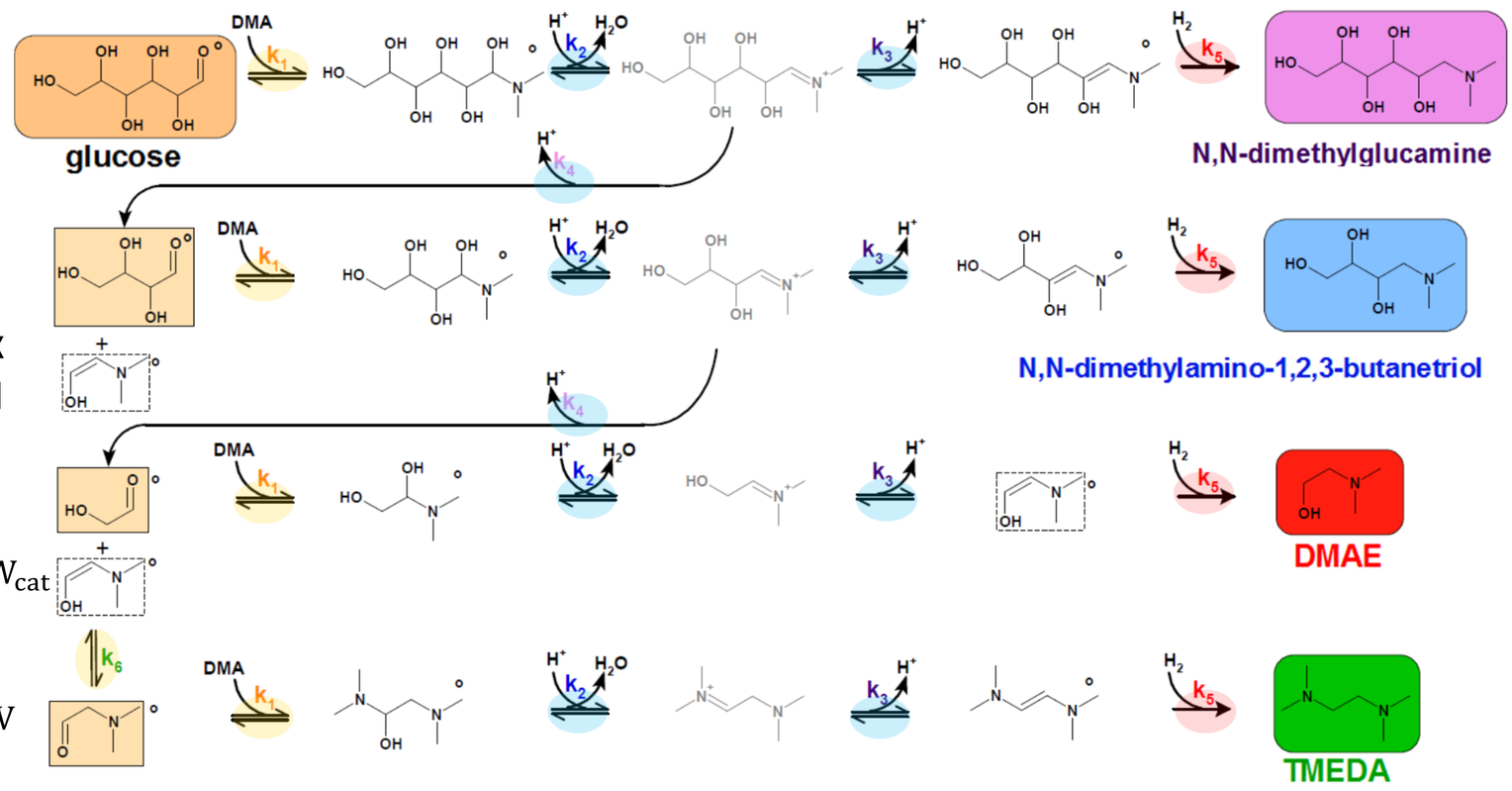
REACTION NETWORK: 3 TYPES OF CATALYSIS

homogeneous base catalysis: 1. amination step; 6. keto-enol tautomerism

heterogeneous acid catalysis ◊: 2. iminium ion formation; 3. enamine rearrangement; 4. retro-aldol

heterogeneous metal catalysis *: 5. enamine hydrogenation

° 7. susceptible to homogeneous degradation



RATE EQUATIONS

$$r_1 = \left(k_1 a_{DMA}^2 a_{glucose} - k_{-1} a_{DMA} a_{hemiC_6}\right)\varepsilon V$$

$$r_2 = \left(k_2 \theta_{\Diamond,hemiC_6} - k_{-2} \theta_{\Diamond,imC_6^+} a_{H_2O}\right) W_{cat}$$

$$r_3 = \left(k_3 \theta_{\Diamond,imC_6^+} - k_{-3} \theta_{\Diamond,enamC_6}\right) W_{cat}$$

$$r_4 = k_4 \theta_{\Diamond,imC_6^+} W_{cat}$$

$$r_5 = k_5 \theta_{\Diamond,enamC_6} \theta_{*,H}^2 W_{cat}$$

$$r_6 = \left(k_6 a_{DMA} a_{enamC_2} - k_{-6} a_{DMA} a_{C_4H_9NO}\right)\varepsilon V$$

$$r_7 = k_7 a_{glucose} \varepsilon V$$

Estimated average rate coefficient				Estimated activation energy (kJ mol^{-1})		
$k_{Tave,1}$	$6.3\ 10^{-10}$	$\pm 0.5\ 10^{-10}$	m_L^6 mol^{-2} s^{-1}	$E_{a,1}$	78.1	± 7.2
$k_{Tave,2}$	$2.1\ 10^{4}$	$\pm 0.6\ 10^{4}$	mol kg_{cat}^{-1} s^{-1}	$E_{a,2}$	49.9	± 4.9
$k_{Tave,3}$	$7.0\ 10^{-2}$	$\pm 1.3\ 10^{-2}$	mol kg_{cat}^{-1} s^{-1}	$E_{a,3}$	47.5	± 7.9
$k_{Tave,4}$	$3.9\ 10^{-1}$	$\pm 0.7\ 10^{-1}$	mol kg_{cat}^{-1} s^{-1}	$E_{a,4}$	59.9	± 9.9
$k_{Tave,5}$	$5.0\ 10^{1}$	$\pm 0.7\ 10^{1}$	mol kg_{cat}^{-1} s^{-1}	$E_{a,5}$	8.8	± 2.5
$k_{Tave,6}$	$8.9\ 10^{-4}$	$\pm 1.2\ 10^{-4}$	m_L^3 mol^{-1} s^{-1}	$E_{a,6}$	1.6	± 0.3
$k_{Tave,7}$	$2.8\ 10^{-3}$	$\pm 0.2\ 10^{-3}$	s^{-1}	$E_{a,7}$	141.7	± 13.0

Estimated average adsorption equilibrium coefficient (m_L^3 mol^{-1})			Estimated adsorption enthalpy (kJ mol^{-1})		
$K_{Tave,C6}$	$5.7\ 10^{-5}$	$\pm 1.0\ 10^{-5}$	$-\Delta H_{ads,C6}$	-30.3	± 9.1
$K_{Tave,C4}$	$6.7\ 10^{-2}$	$\pm 0.6\ 10^{-2}$	$-\Delta H_{ads,C4}$	-13.7	± 1.9
$K_{Tave,C2}$	$7.0\ 10^{-3}$	$\pm 0.3\ 10^{-3}$	$-\Delta H_{ads,C2}$	-26.0	± 4.6
$K_{Tave,H2}$	1.1	± 0.3	$-\Delta H_{ads,H2}$	-2.9	± 0.3

statistically significant model: $F_{test} = 160 > F_{tab} = 2.79$

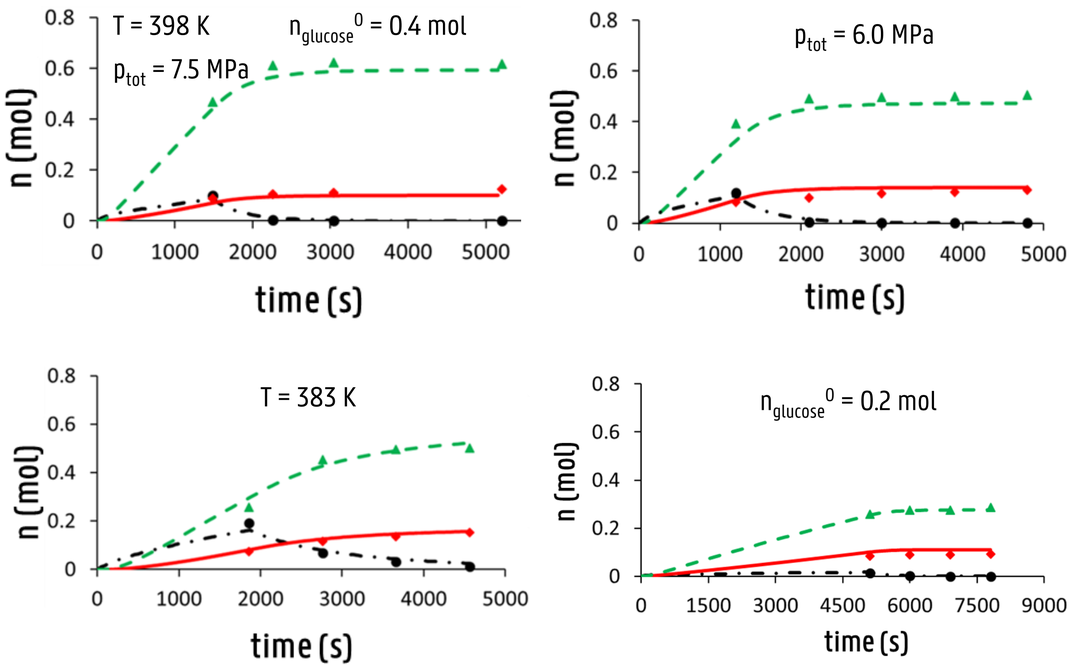
KINETIC MODEL

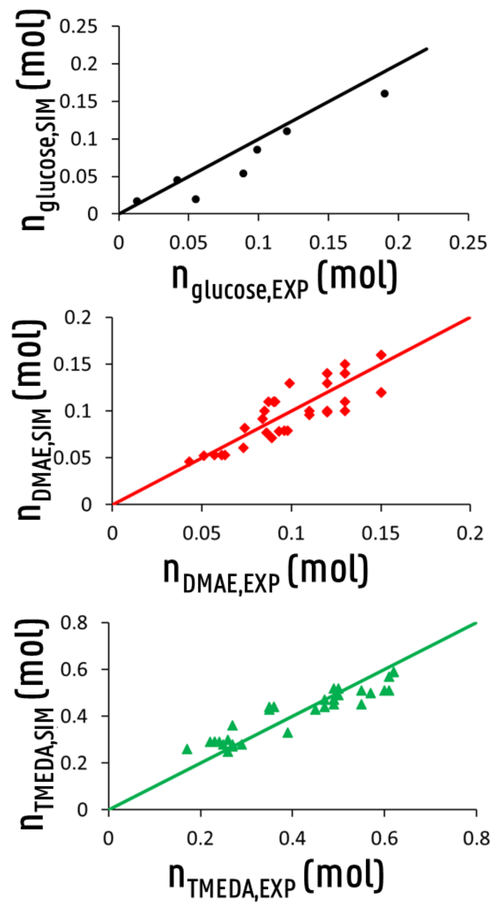
higher temperatures favor retro-aldol cleavage and thus DMAE and TMEDA formation

$E_{a,4}$ significantly lower than typical retro-aldol ~ 140 kJ mol^{-1} → retro-aldol below 400K

selectivity tuning between DMAE and TMEDA not possible by varying the temperature

too high temperatures result in almost exclusively degradation products





CONCLUSIONS

renewable and **safe** production route for DMAE and TMEDA **without excessive degradation**

activation energy for retro-aldol ($E_{a,4}$) is significantly reduced by the presence of a nitrogen atom →retro-aldol occurs at temperatures below 400 K

statistically significant **kinetic model** manages to **simulate and explain experimentally observed trends**

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